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CERAMIC AND VITREOUS MATERIALS BASED ON PLAGIOCLASE

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The possibility of obtaining various pigments by replacing some of the aluminum oxide in basic batch by chromium or iron oxide is shown.

Plagioclases form a continuous series of isomorphous mixtures [1] of albite $\text{Na}[\text{AlSi}_3\text{O}_8]$ and anorthite $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$. The minerals of this series are used as decorative stones and as material components for ceramic, glass ceramic, and devitrified materials [2–5]. The authors investigated these minerals in order to have a fuller understanding of the potential of their use in synthesis of ceramic and vitreous materials.

Several composites were synthesized whose stoichiometric composition corresponds to isomorphous mixtures of albite and anorthite: albite Ab_{100} , oligoclase $\text{Ab}_{80}\text{An}_{20}$, andesine $\text{Ab}_{60}\text{An}_{40}$, labrador $\text{Ab}_{40}\text{An}_{60}$, bytownite $\text{Ab}_{20}\text{An}_{80}$, anorthite An_{100} .

The batches were prepared using as the reactants Na_2CO_3 , CaO , Al_2O_3 or $\text{Al}(\text{OH})_3$, SiO_2 , Cr_2O_3 , and Fe_2O_3 of grades "pure," "chemically pure," "extra pure." In some

cases SiO_2 was introduced as sand used in glass production (SiO_2 content over 99.5%)

Batch components were mixed in a porcelain mortar and underwent primary heat treatment in an MP-2UM muffle furnace (1000°C, 1 h). After crushing and milling (1.5–2 h), the materials were compressed (a pressure up to 8 MPa). The resulting cylindrical samples approximately 21 mm in diameter and up to 40 mm high were treated in an Émitron SVK5163 high-temperature furnace in the temperature range of 1100–1400°C. After a temperature rise by every 100°C, the samples were held for 1 h. The heat-treatment results are evaluated by the change in the diameter.

An x-ray phase analysis was performed using a DRON-3M diffractometer (copper radiation). The TCLE was measured on a DKV-4a vertical quartz dilatometer. The chemical resistance was found from the weight loss after

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TABLE 1

Composite	Component for introducing SiO_2	Temperature, °C			
		1100	1200	1300	1400
Ab_{100}	Amorphous SiO_2 Sand		SiO_2 (cryst.) SiO_2 (quartz)		X-ray amorphous
$\text{Ab}_{80}\text{An}_{20}$	Amorphous SiO_2	SiO_2 (cryst.) and $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ (rhomb.)			The same
$\text{Ab}_{60}\text{An}_{40}$	The same	SiO_2 (cryst.) and $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ (rhomb.)			"
		$\text{Ca}_2\text{Al}[\text{AlSiO}_7]$ and $\gamma\text{-Al}_2\text{O}_3$		–	"
$\text{Ab}_{40}\text{An}_{60}$	"	SiO_2 (cryst.) and $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ (rhomb.)			"
		$\text{Ca}_2\text{Al}[\text{AlSiO}_7]$ and $\gamma\text{-Al}_2\text{O}_3$		–	"
	Sand	SiO_2 (cryst.) and $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ (rhomb.)			"
		Formation of Al_2O_3 (corundum) and $\gamma\text{-Al}_2\text{O}_3$ is possible			"
$\text{Ab}_{20}\text{An}_{80}$	Amorphous SiO_2	SiO_2 (cryst.), $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ (rhomb.), $\text{Ca}_2\text{Al}[\text{AlSiO}_7]$, and $\gamma\text{-Al}_2\text{O}_3$		$\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ (tricl.)	
An_{100}	The same	The same			The same
	Sand	SiO_2 (quartz)		$\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ (tricl.)	
		–	Formation of Ca_2SiO_4 and Al_2O_3 (corundum) is possible		–

boiling grains of the fraction 0.3 – 0.5 mm in distilled water for 1 h.

The sintering of the composite corresponding to albite starts at a relatively low temperature. A high-quality cake is formed at the initial temperature of the synthesis, i.e. at 1000°C.

When the temperature is increased to 1200 and 1300°C, the sample diameters become significantly smaller, but the overall reduction does not exceed 12%. The average residual sample diameters are as follows (%): $\text{Ab}_{80}\text{An}_{20}$ 90.6 (1100 and 1200°C), $\text{Ab}_{60}\text{An}_{40}$ 95.1 (1100 – 1300°C), $\text{Ab}_{40}\text{An}_{60}$ 99.4 (1100 – 1300°C), $\text{Ab}_{20}\text{An}_{80}$ 88.9 (1200 and 1300°C). The composite corresponding to anorthite exhibits an insignificant diameter increase over the whole temperature interval (1100 – 1400°C), which is equal to 1.8% on the average.

The x-ray phase analysis data are shown in Table 1. It can be seen that as the CaO content increases, the number of crystalline phases grows and their composition becomes more complex. Furthermore, with increasing CaO content in the composites, the amount of the amorphous phase in heat treatment decreases, and the melting point become higher. This is due to the fact that with increasing CaO content, the possibility of formation of various crystalline modifications of anorthite is manifested to a greater extent. As can be seen from the phase diagram of anorthite [6], in this case melt formation can be expected at a temperature of 1550°C.

The degree of sintering of the samples increases and the melting point decreases with increasing Na_2O content. The TCLE of the samples does not exceed $75.3 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$, the weight loss in water is within the limits of 0.2 to 0.3%. Compact and well-sintered samples of the composite corresponding to albite can be obtained at a temperature of 1100°C.

In order to synthesize pigments in composites corresponding to albite, some of the aluminum oxide was replaced by chromium or iron oxide (Table 2).

Mixtures of the batch components after compression were treated at a temperature of 950°C. The samples containing Cr_2O_3 were held 1 h, and the samples containing Fe_2O_3 were held 0.5 h. In the case of Cr_2O_3 the pigments had a greenish tint, and in the case of Fe_2O_3 the tint was brownish. On introducing these pigments (6 wt.%) into vitreous $\text{Ba}(\text{PO}_3)_2$, high-quality glasses of the same tint were obtained.

Subsequently, the molar content of Cr_2O_3 and Fe_2O_3 was increased to 10 and 15% (Table 3).

Mixtures of the batch components after compression were held at temperatures of 1000°C (composites 5 and 6) and 900°C (composites 7 and 8). The samples containing Cr_2O_3 exhibited only sintering, and the samples containing Fe_2O_3 revealed partial formation of melts. The color tone of

TABLE 2

Composite	Molar content, %*				Weight content, %			
	Al_2O_3	Cr_2O_3	Fe_2O_3	Na_2O	Al_2O_3	Cr_2O_3	Fe_2O_3	SiO_2
1	22.5	2.5	—	21.44	31.74	5.26	—	41.56
2	20.0	5.0	—	20.35	30.16	9.98	—	39.51
3	22.5	—	2.5	21.37	31.66	—	5.51	41.46
4	20.0	—	5.0	20.95	27.60	—	10.80	40.65

* All composites contained 25% Na_2O and 50% SiO_2 .

TABLE 3

Composite	Molar content, %*				Weight content, %			
	Al_2O_3	Cr_2O_3	Fe_2O_3	Na_2O	Al_2O_3	Cr_2O_3	Fe_2O_3	SiO_2
5	15	10	—	20.37	20.12	19.98	—	39.53
6	10	15	—	19.72	12.98	29.03	—	38.27
7	15	—	10	20.17	19.91	—	20.82	39.10
8	10	—	15	19.43	12.80	—	30.06	37.71

* All composites contained 25% Na_2O and 50% SiO_2 .

TABLE 4

Composite	Molar content, %*				Weight content, %				
	Na_2O	CaO	Al_2O_3	Fe_2O_3	Na_2O	CaO	Al_2O_3	SiO_2	Fe_2O_3
9	12.50	12.50	18.75	6.25	10.08	9.54	25.98	40.84	13.56
10	12.50	12.50	12.50	12.50	9.62	9.08	16.52	38.92	25.86
11	—	25.00	18.75	6.25	—	19.16	26.14	41.06	13.64
12	—	25.00	12.50	12.50	—	18.26	16.61	39.13	26.00

* All composites contained 50% SiO_2 .

the samples did not change significantly, but became perceptibly more intense.

Table 4 shows the compositions of composites in which half or all the Na_2O is replaced by CaO. Accordingly, their composition approaches the composition of anorthite. In all the composites 6.25 or 12.50 mole% Al_2O_3 was replaced by 6.25 or 12.50% Fe_2O_3 .

After compression and firing at a temperature of 1000°C (0.5 h), the samples containing Na_2O had the form of brownish sinters. When the Fe_2O_3 content was increased, the color intensity became significantly higher. The samples containing only CaO remained loose at this temperature, but the reaction products had a red-brown color, whose intensity increased with increasing Fe_2O_3 content.

The results obtained can be used to synthesize ceramic and vitreous materials.

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